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ADVANCED CALCIUM-THIONYL CHLORIDE HIGH-POWER BATTERY
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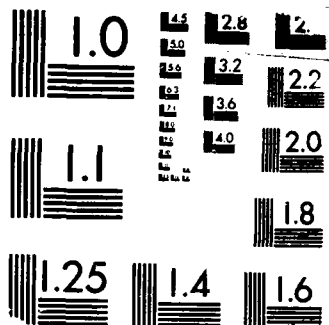
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ADVANCED CALCIUM-THIONYL CHLORIDE HIGH-POWER BATTERY

Periodic Technical Report

by

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Prof. E. Peled

First Periodic Report

(December 1987-February 1988)

United States Army

EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY

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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) Recently we at TAU have made a breakthrough in the development of two advanced Ca-TC systems which have much better storage properties than the state-of-the-art Ca- SOCl_2 cell. This has been done by replacing the CaX_2 ($\text{X}=\text{AlCl}_4$) electrolyte by SrX_2 (type A), or BaX_2 (type B). The project's goals are to gain a better understanding of the electrochemistry of the advanced systems and to establish their safety and performance. In this first report we present preliminary results regarding the properties of these three electrolytes emphasizing the role of SO_2 in affecting their viscosity, conductivity and Raman spectra. | | | | | |
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Introduction

Recently we, at TAU, have made a breakthrough in the development of two advanced Ca-TC systems (1,2,3) which have much better storage properties than the state-of-the-art Ca cell. These are: $\text{Ca/Sr(AlCl}_4)_2\text{-SOCl}_2/\text{C}$ - (type A) and $\text{Ca/Ba(AlCl}_4)_2\text{-SOCl}_2/\text{C}$ - (type B). Our modified (but not optimized) C-size hermetically sealed cell delivered 4.4 Ah after one month of storage at 70°C. This is 10-20% higher than the capacity of a fresh Li-SO₂ C-size cell.

The project's goals are to gain a better understanding of the electrochemistry of the advanced calcium-thionyl chloride system and to establish the safety and performance properties of optimized C-size hermetically sealed cells with the use of our proprietary art.

We expect that our advanced calcium battery will have 25-50% more capacity than a similar size Li-SO₂ battery. Our Ca-TC cell can be made vent-free and able to resist, with no rupture or leakage, abuse tests including forced discharge, charging, mechanical damage and short circuit (under certain conditions). Thus no limitations on air transportation are expected. Its shelf-life is expected to be 3-5 years at 20°C and its operating temperature range is -30 (or even -40) to 150-200°C, depending on the rate of discharge.

The Ca-TC cell has a working voltage equal to that of the Li-SO₂ cell. Thus, it can replace the Li-SO₂ battery with no problem. In addition it is expected to be less expensive than the Li-SO₂ technology.

We believe that our advanced Ca-TC technology, after being fully developed, can be used as the major power source for all portable electronic equipment in the army. It will give better performance, better safety and lower cost than is offered by the existing Li-SO₂ technology.

The proposed statement of work includes: study of the electrochemistry, safety, performance and storage properties of the state- of-the-art $\text{Ca/Ca(AlCl}_4)_2\text{-TC+SO}_2\text{/C}$ system as a baseline system, and of our two advanced modified systems A and B. In modification A, we have changed the chemical composition of the Solid Electrolyte Interphase (SEI) of the calcium, and in modification B, we mainly changed the morphology and decreased the thickness of the SEI (1-3). We would like to accomplish a better understanding of the effects of SEI chemical composition, morphology and electrochemical properties on the performance, safety and storage properties of the Ca-TC sealed battery. The experimental techniques that will be used include conductivity measurements, Raman spectroscopy and viscosity measurements on the electrolytes; AC, SEM, micro-calorimetry, calorimetry of the electrochemical cells and cell components as well as storage, discharge and safety tests of sealed cells. The time frame is three years.

Experimental

All solutions were prepared and handled inside an argon-filled glove box. Riedel AR $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was vacuum dried at 130°C for 24h. It was mixed with AlCl_3 (Fluka Puriss)- SOCl_2 (Merck Zur Synthesis) solution to give the desired $\text{Sr(AlCl}_4)_2$ concentration. The resulting solution (with 10% excess of solid SrCl_2) was refluxed with calcium strips for 24h. The exact concentrations of Al and Sr were determined by atomic absorption (Perkin Elmer 403). The Al:Sr atomic ratio was found to be 2:1. Sulfur dioxide gas (Matheson 99.98%) was added to these solutions with the use of vacuum line. The final SO_2 concentration was determined from weight change. The solution conductivity was measured with the use of a four-platinum-electrode ampoule (shown in Fig.1) and El-Hama model TH 230 conductivity meter. This cell was designed to withstand a pressure of 10At. Sulfur dioxide was added directly

to the solution in the conductivity cell with the use of a vacuum line.

The viscosity of the solutions was measured with the use of a Lewis Viscosimeter (shown in Fig.2) over a temperature range of 10 to 70°C. A Rotaflo Teflon valve was attached to this viscosimeter and through it solution and SO₂ gas were introduced. The addition of SO₂ was accomplished with the use of a vacuum line.

Raman spectroscopy measurements were carried out (at Ben Gurion University with Prof. S. Efrima) with the use of glass ampoules similar in shape and size to the conductivity cells. The details of the Raman spectrophotometer: Coherent Innova Laser model 90/4; the excitation wave length was 514nm; Spex model 1403 monochromator, RCA type C31034 photomultiplier; "OSMA" - Optical Spectroscopic Multichannel Analyser; P.I. type ST120 detector; P.I. type ST120 Controller and IBM AT computer which controls "OSMA", reads and processes the data. The typical resolution of this system was 5 cm⁻¹.

AC measurements were conducted with the use of a home-made system which consists of an IBM PC-XT computer equipped with a Tecmar A/D board (TM40) and a home-made galvanostat. Frequency response range is 0.001 Hz to 10,000 Hz. The electrochemical cell consists of a hermetically sealed C-size SS cell with two G/M feedthroughs (one in the bottom and one in the cover) to which the calcium reference and working electrodes were attached. A round porous-nickel counter electrode was connected to the can.

RESULTS AND DISCUSSIONS

1. Electrolyte Properties

a) Sr(AlCl₄)₂ - TC - SO₂ system.

This project is the continuation of many years of effort in our laboratory. Its goal is a better understanding of the conduction mechanisms

in TC/electrolytes and the effect on them of SO_2 and temperature. In addition, we would like to form a data base which will help in optimizing the Ca-TC battery.

The effects of SO_2 and temperature on the conductivity of 0.84M $\text{Sr}(\text{AlCl}_4)_2$ - TC solutions are shown in Fig. 3 (Ref.3). There is a pronounced effect of SO_2 (up to a factor of 7 at low temperatures) on the conductivity.

In order to understand the reasons for this conductivity enhancement we conducted viscosity and Raman spectroscopy tests. The effects of SO_2 and temperature on the viscosity of 0.84M $\text{Sr}(\text{AlCl}_4)_2$ -TC- SO_2 solutions are shown in Fig.4. It is interesting to note that increasing SO_2 concentration from 0 to 10% does not significantly alter the solution viscosity. The conductivity corrected for the change in viscosity increases with the rise of SO_2 concentration from 0 to 10% and does not change with further increase in SO_2 concentration.

Raman spectra of 30% SO_2 - TC-0.84M $\text{Sr}(\text{AlCl}_4)_2$ (Fig.5) taken at room temperature (Ref. 3) indicates the formation of a complex between SO_2 and Sr^{++} . The peak at 1140 cm^{-1} is assigned to SO_2 while the peak at 1147 cm^{-1} is assigned to the $\text{Sr}(\text{SO}_2)_n^{++}$ complex). The $\text{Sr}(\text{SO}_2)_n^{++}$ peak height increases with SO_2 concentration. It seems that the maximum value of n is three (Ref.3). These results indicate that the conductivity enhancement at low SO_2 concentration is predominantly due to the formation of a larger SO_2 - Sr^{++} complex ion (or an aggregate of of such ions) and at high concentration is due to the decrease in the viscosity of the electrolytes.

b) $\text{Ca}(\text{AlCl}_4)_2$, $\text{Ba}(\text{AlCl}_4)_2$ -TC- SO_2 systems.

Preliminary results regarding viscosity and Raman spectroscopy measurements are reported here. The effect of SO_2 on viscosity of 1M

$\text{Ca}(\text{AlCl}_4)_2$ can be seen in Fig. 6. The effect of 20% SO_2 on the viscosity of some Sr, Ca and Ba solutions can be estimated by comparing figures 7 and 8.

Raman spectra of 1M $\text{Ca}(\text{AlCl}_4)_2$ 30% SO_2 -TC solution (Fig.9) indicate formation of a SO_2 complex as shown by the appearance of a shoulder or small peak at 1149 cm^{-1} .

Further results and discussions will be submitted in the next report.

2. AC MEASUREMENTS

The AC spectrum (Cole-Cole plot) for $\text{Ca}/\text{Ca}(\text{AlCl}_4)_2$ - SOCl_2 system has been previously measured in our laboratory (Ref. 4) over a frequency range of 40 Hz to 80 kHz. We have now extended these measurements to low frequencies - down to 0.001 Hz. A typical AC spectrum for the calcium-SEI electrode is given in Fig.10. The upper (positive) arc has a somewhat depressed shape. R_1 and R_2 increase with storage time but the ratio R_1/R_2 decreases. The upper arc is assigned to the SEI resistance while the lower one is probably associated with the ionic transference numbers in the SEI. The SEI resistivity (ρ) is, to a first approximation, calculated from W_{\max} of the upper curve:

$$\rho = \frac{1}{W_{\max} \epsilon \epsilon_0}$$

where ϵ_0 and ϵ are the permittivity of vacuum and the dielectric constant of the CaCl_2 SEI respectively, ($\epsilon = 6$). The apparent thickness of the SEI (ℓ) is calculated from:

$$\ell = \epsilon \epsilon_0 \frac{A}{C}$$

where A - electrode area, and C - electrode capacitance. The characteristics of the Ca-SEI electrode in $\text{Ca}(\text{AlCl}_4)_2$ -TC solutions are summarized in Table 1.

TABLE 1

| | Meitav/Peled* (Ref. 4) | This Work ** |
|---|---------------------------|----------------------|
| Capacity, $\mu\text{F}/\text{cm}^2$ | 0.18 | 0.11 |
| SEI app. thickness, (\AA) | 490 | 485 |
| Electrode resistance, $k_{\text{ohm}} \text{ cm}^2$ | 66 | 36 |
| SEI resistivity (ρ), ohm cm | 1.3×10^{10} | $0.74 \cdot 10^{10}$ |

* Two months of storage in 0.9M $\text{Ca}(\text{AlCl}_4)_2$.

** One month of storage in 0.75M $\text{Ca}(\text{AlCl}_4)_2$.

3. C-SIZE CELL ASSEMBLY

Nine C-size Ca-TC cells have been assembled. They have 130 cm^2 of active electrode area and consist of: calcium anode pfizer 99.9% ($0.5 \times 210 \times 40 \text{ mm}$), porous carbon cathode ($0.7 \times 200 \times 40 \text{ mm}$), 0.9M $\text{Ca}(\text{AlCl}_4)_2$ + 7% SO_2 . These cells will be tested during the next period.

4. Research Plans for Remainder of the Contract Period.

1. Baseline system $(\text{Ca}(\text{AlCl}_4)_2 - \text{TC})$.
 - 1.1. Complete the Raman and viscosity measurements for the $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2\text{-SO}_2$ system.
 - 1.2. Study the effect of SO_2 on the calcium-SEI electrode.
 - 1.3. Evaluate the properties of C-size baseline cells.
2. Study the electrochemistry of type A and B systems $\text{Sr}(\text{AlCl}_4)_2\text{-SOCl}_2\text{-SO}_2$ and $\text{Ba}(\text{AlCl}_4)_2\text{-SOCl}_2\text{-SO}_2$.
 - 2.1. Complete the Raman and viscosity measurements.
 - 2.2. Study the effect of SO_2 on the SEI calcium electrode.
 - 2.3. Evaluate the properties of C-size cells having type A electrolyte.

REFERENCES

1. Israel Pat. Appl. No. 77786, UK Pat. Appl. No. GB 2187590A.
2. E. Elster, R. Cohen, M. Brand, Y. Lavi and E. Peled.
Proceedings of the 172nd Electrochemical Soc. Meeting, Honolulu 1987.
3. E. Elster, R. Cohen, M. Brand, Y. Lavi and E. Peled
J. Electrochem. Soc. in press.
4. A. Meitav and E. Peled, Electrochimica Acta, in press.

Figure Captions

- Fig. 1. Conductivity Cell.
- Fig. 2. Lewis Viscometer.
- Fig. 3. Conductivity of 0.84M $\text{Sr}(\text{AlCl}_4)_2$ - SO_2 -TC solutions vs. temperature.
- Fig. 4. Viscosity of 0.84M $\text{Sr}(\text{AlCl}_4)_2$ - SO_2 -TC solutions vs. temperature.
- Fig. 5. Raman spectrum of 0.84M $\text{Sr}(\text{AlCl}_4)_2$ in TC containing 30% (v/v) SO_2 at room temperature.
- Fig. 6. Viscosity of 1M $\text{Ca}(\text{AlCl}_4)_2$ - SO_2 -TC solutions: 1-0% SO_2 ; 2-20% SO_2 ; 3-30% SO_2 .
- Fig. 7. Viscosity of MX_2 -TC solutions, M = alkali metal, X = AlCl_4^- :
1-0.84M BaX_2 ; 2-0.84M SrX_2 ; 3-1M CaX_2 ; 4-1.3M BaX_2 ; 5-1.3M SrX_2 .
- Fig. 8. Viscosity of MX_2 -TC+20% (v/v) SO_2 solutions as in Fig. 7.
- Fig. 9. Raman spectrum of 1M $\text{Ca}(\text{AlCl}_4)_2$ -TC+30% (v/v) SO_2 at room temperature.
- Fig. 10. An AC spectrum for Ca electrode in 0.75M $\text{Ca}(\text{AlCl}_4)_2$ - SOCl_2 solution after four days of storage at room temperature.

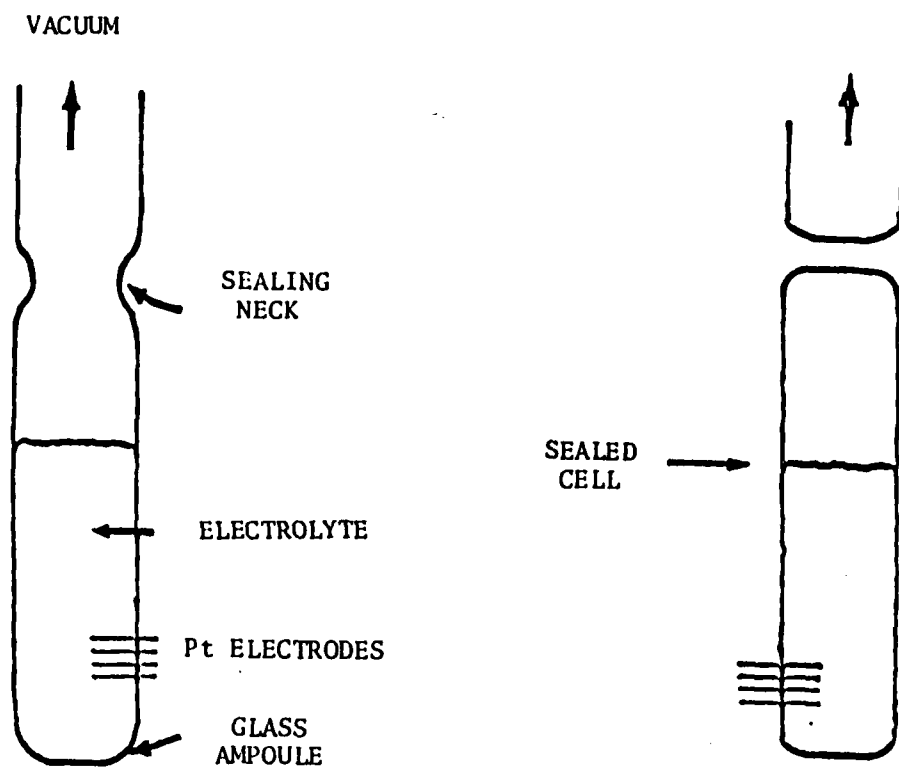


Fig. 1. Conductivity Cell

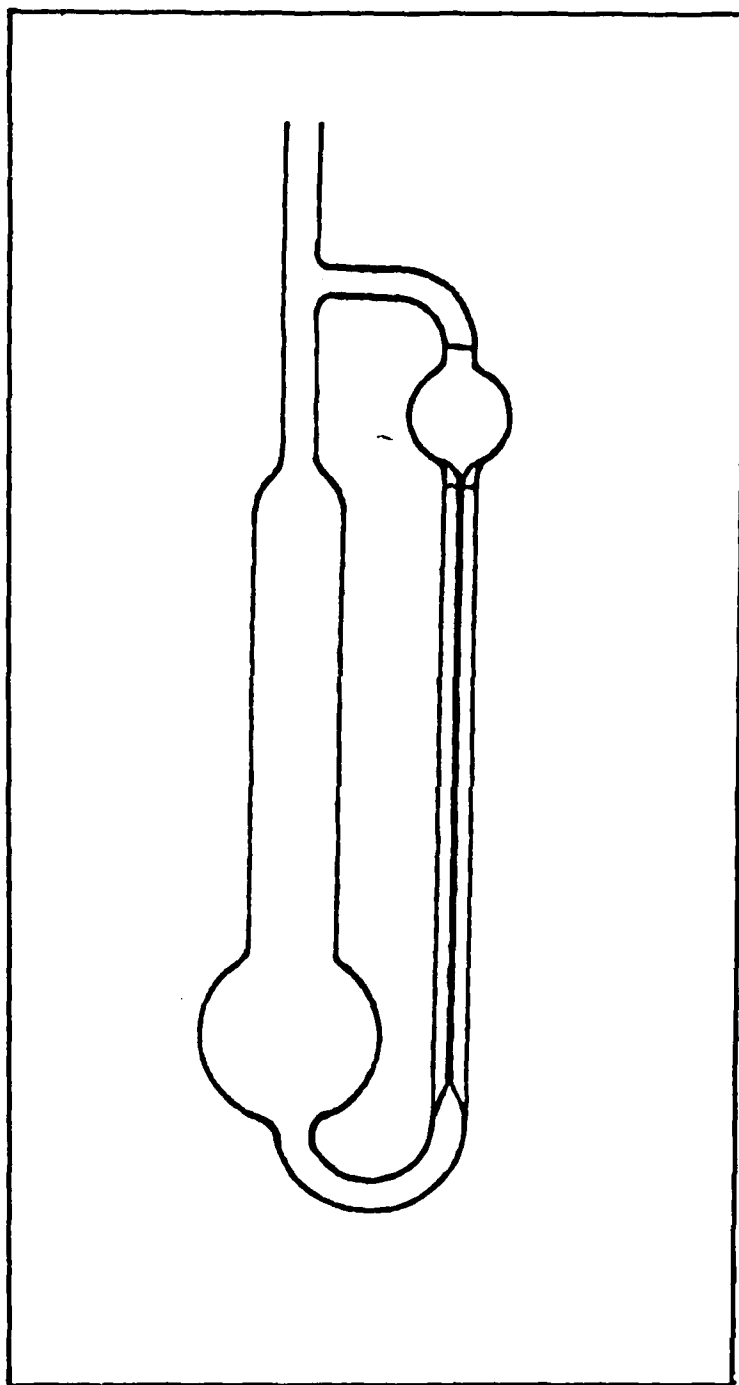


Fig. 2. Lewis Viscometer

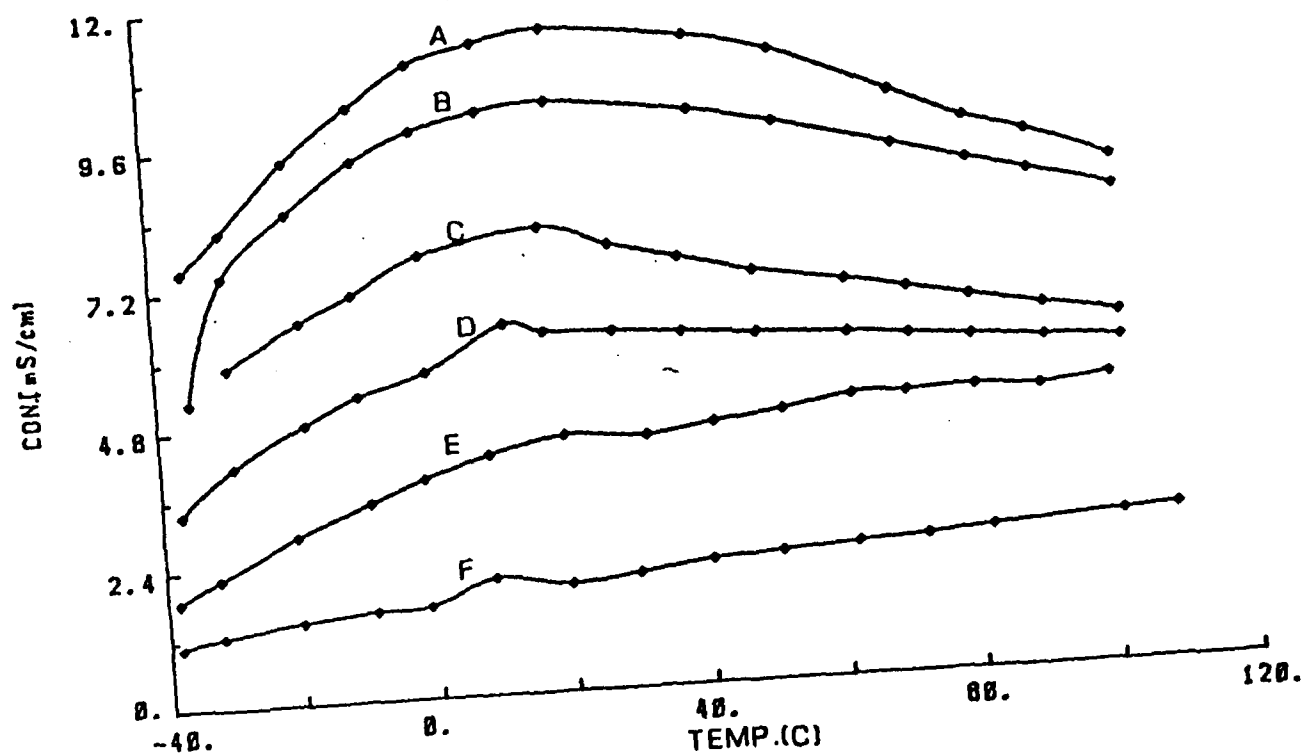


Fig. 3. Conductivity of 0.84M $\text{Sr} (\text{AlCl}_4)_2\text{-SO}_2\text{-TC}$ solutions vs. temperature.

A: 50% SO_2 , B: 40% SO_2 , C: 30% SO_2

D: 20% SO_2 , E: 10% SO_2 , F: 0% SO_2

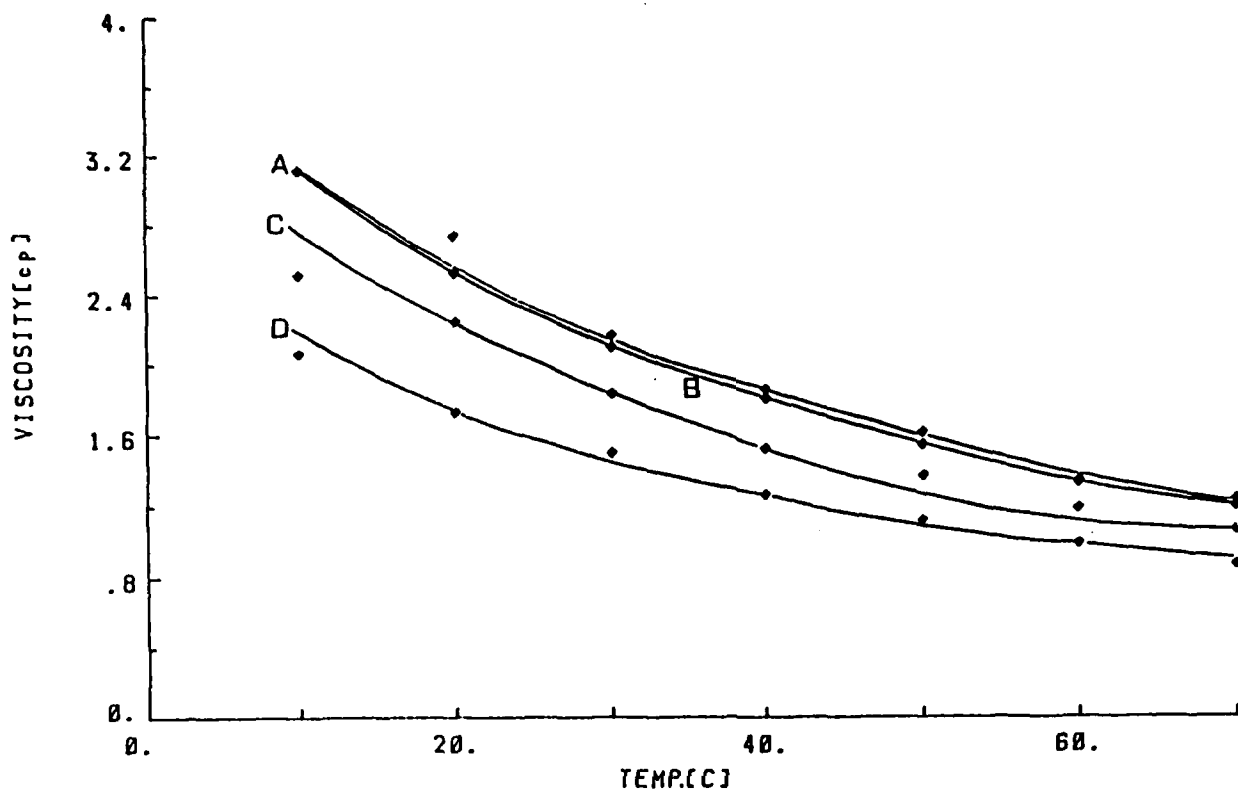


Fig. 4. Viscosity of 0.84M $\text{Sr}(\text{AlCl}_4)_2\text{-SO}_2\text{-TC}$ solutions vs. temperature.

A: 0% SO_2 , B: 10% SO_2

C: 20% SO_2 , D: 30% SO_2

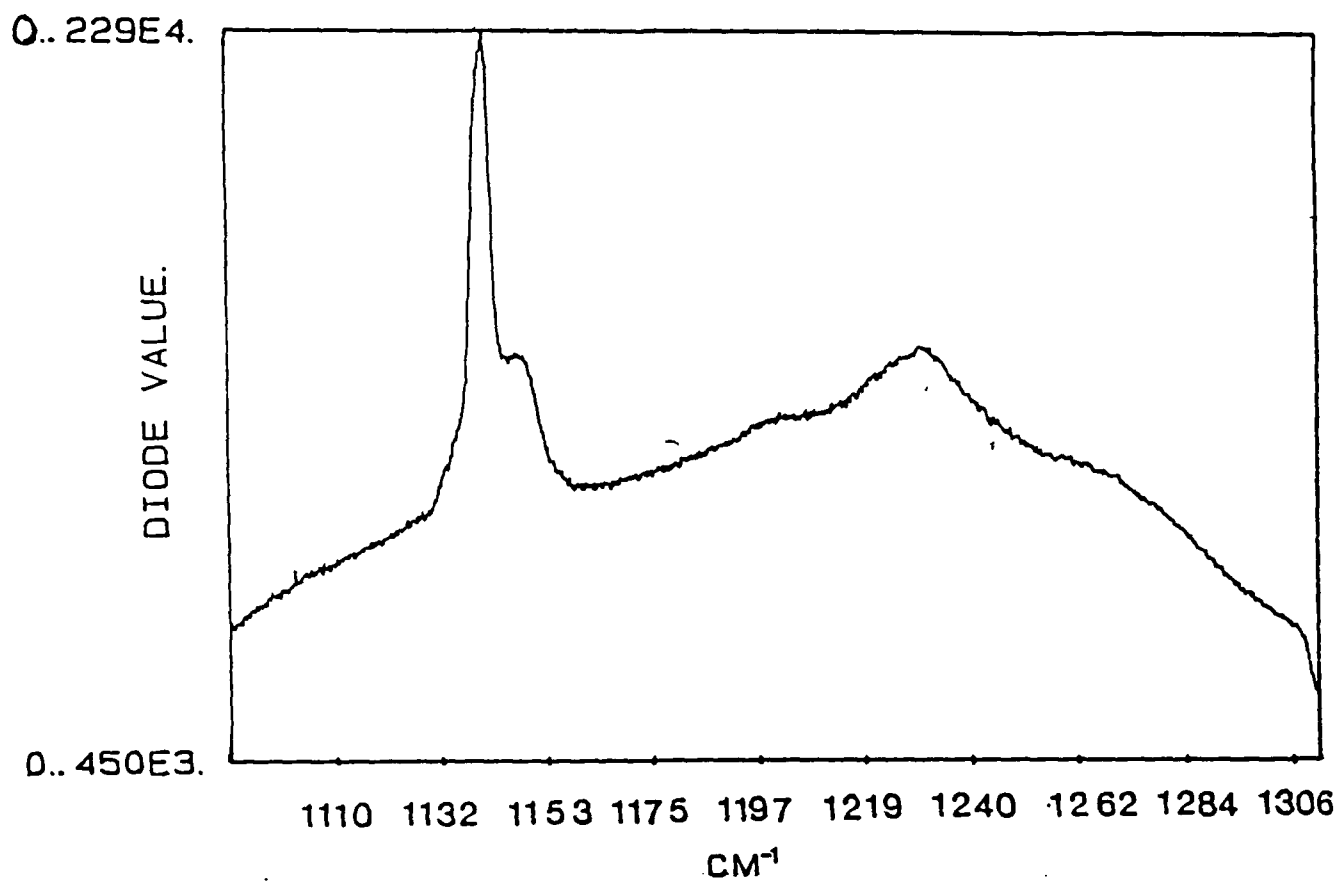


Fig. 5. Raman spectrum of 0.84M $\text{Sr}(\text{AlCl}_4)_2$ in TC containing 30% (v/v) SO_2 at room temperature.

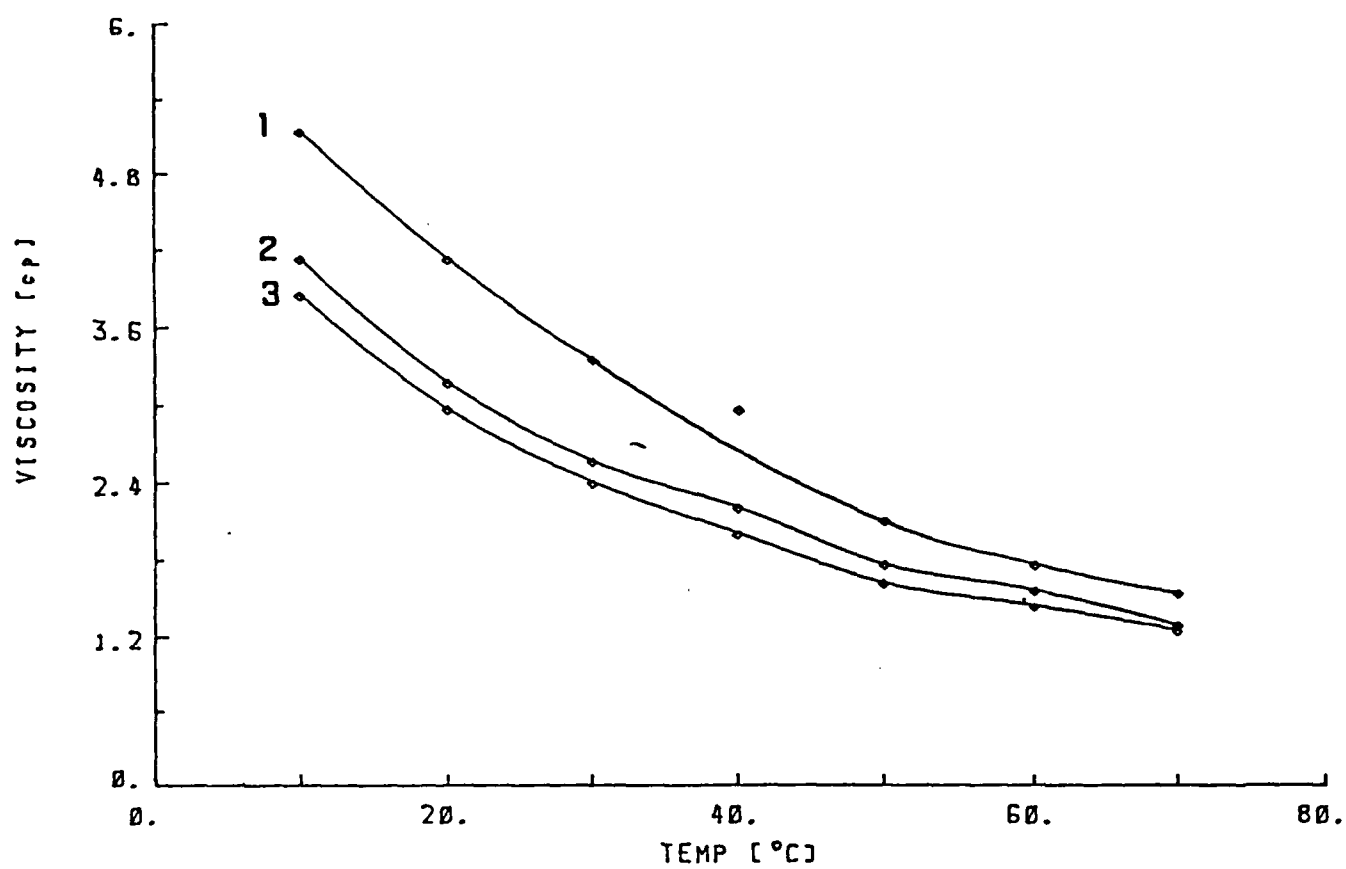


Fig. 6. Viscosity of 1M $\text{Ca}(\text{AlCl}_4)_2$ - SO_2 -TC solutions:
1-0% SO_2 ; 2-20% SO_2 ; 3-30% SO_2 .

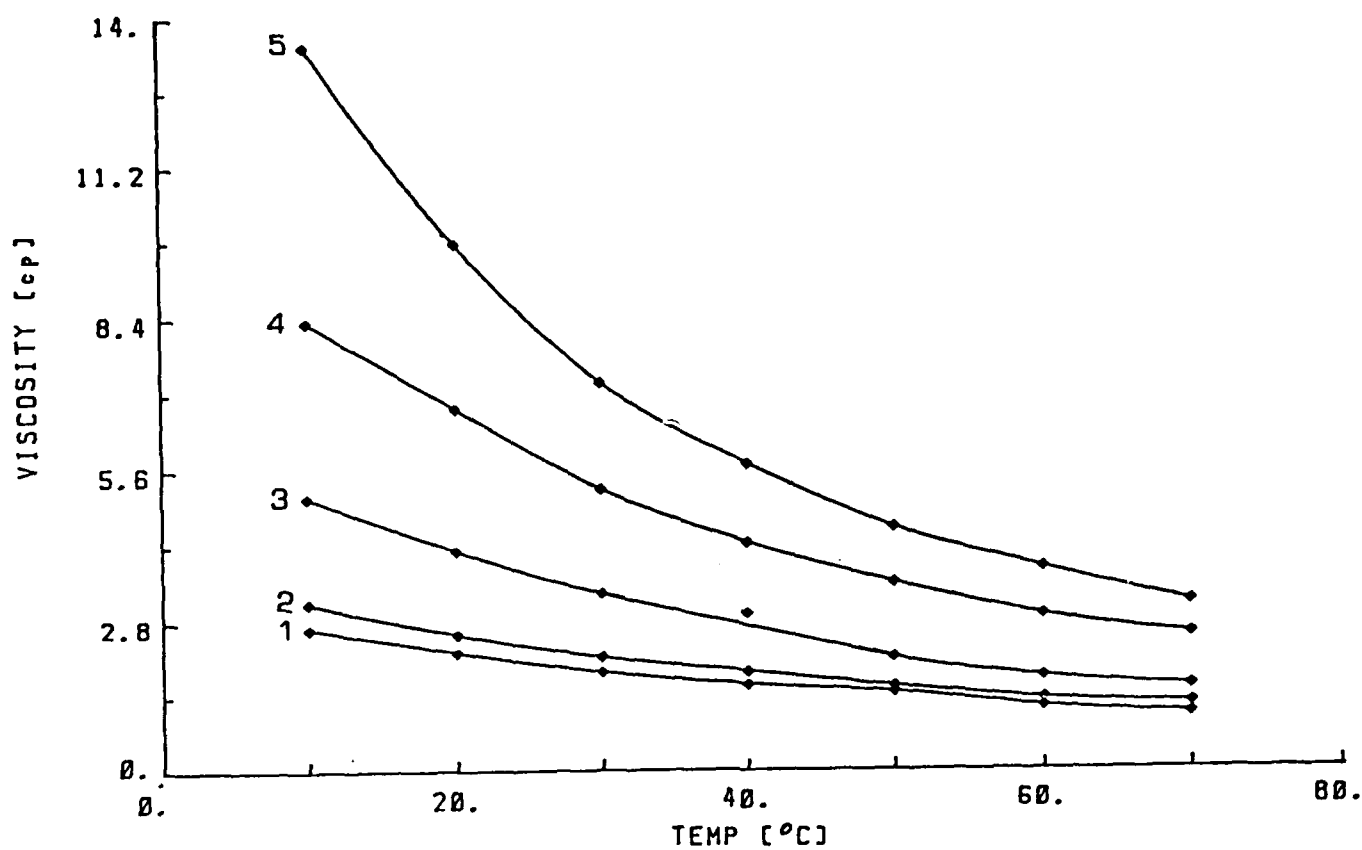


Fig. 7. Viscosity of MX_2 -TC solutions, M = alkali metal,
 $X = AlCl_4^-$: 1-0.84M BaX_2 ; 2-0.84M SrX_2 ;
 3-1M CaX_2 ; 4-1.3M BaX_2 ; 5-1.3M SrX_2 .

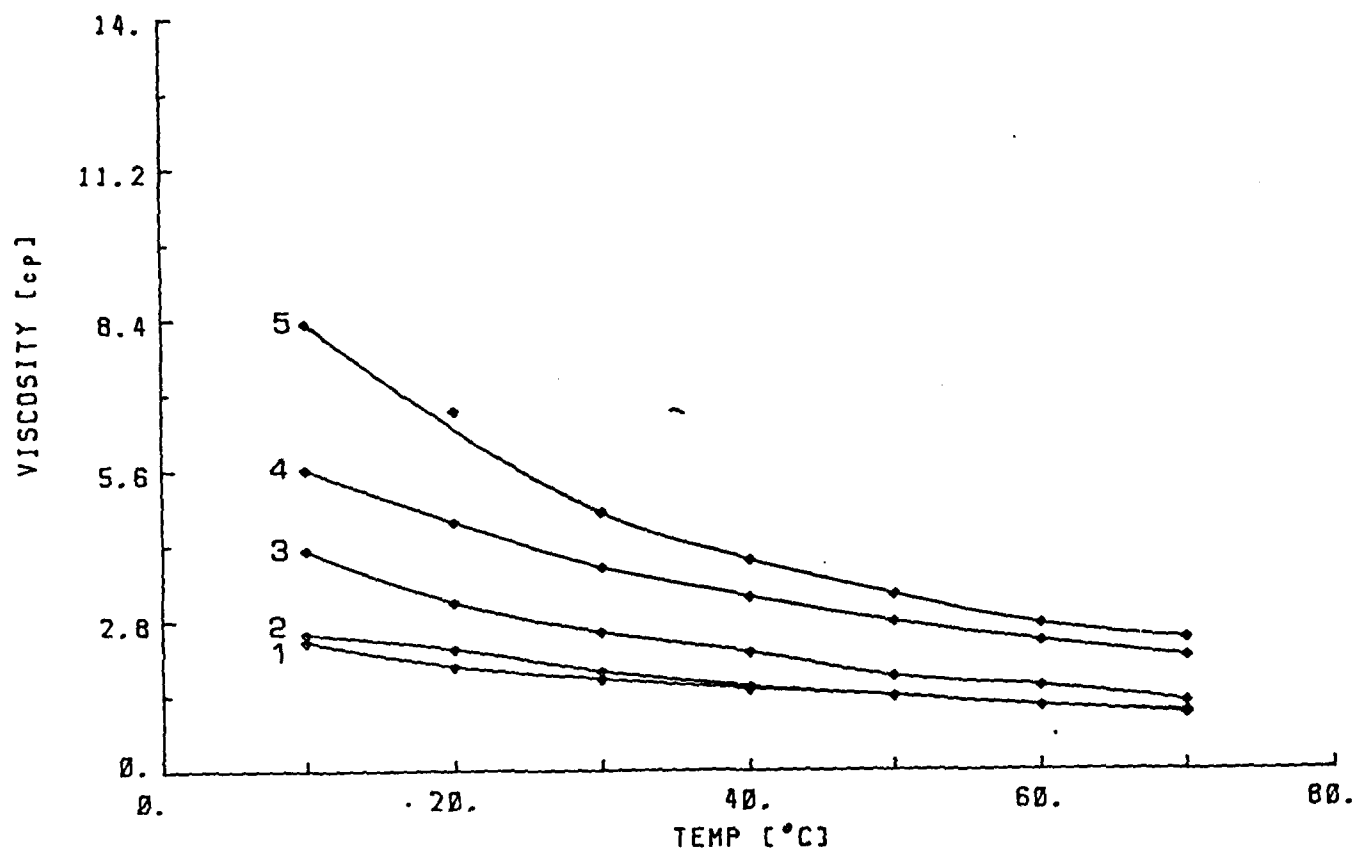


Fig. 8. Viscosity of $\text{MX}_2\text{-TC}+20\%$ (v/v) SO_2 solutions,
as in Fig. 7.

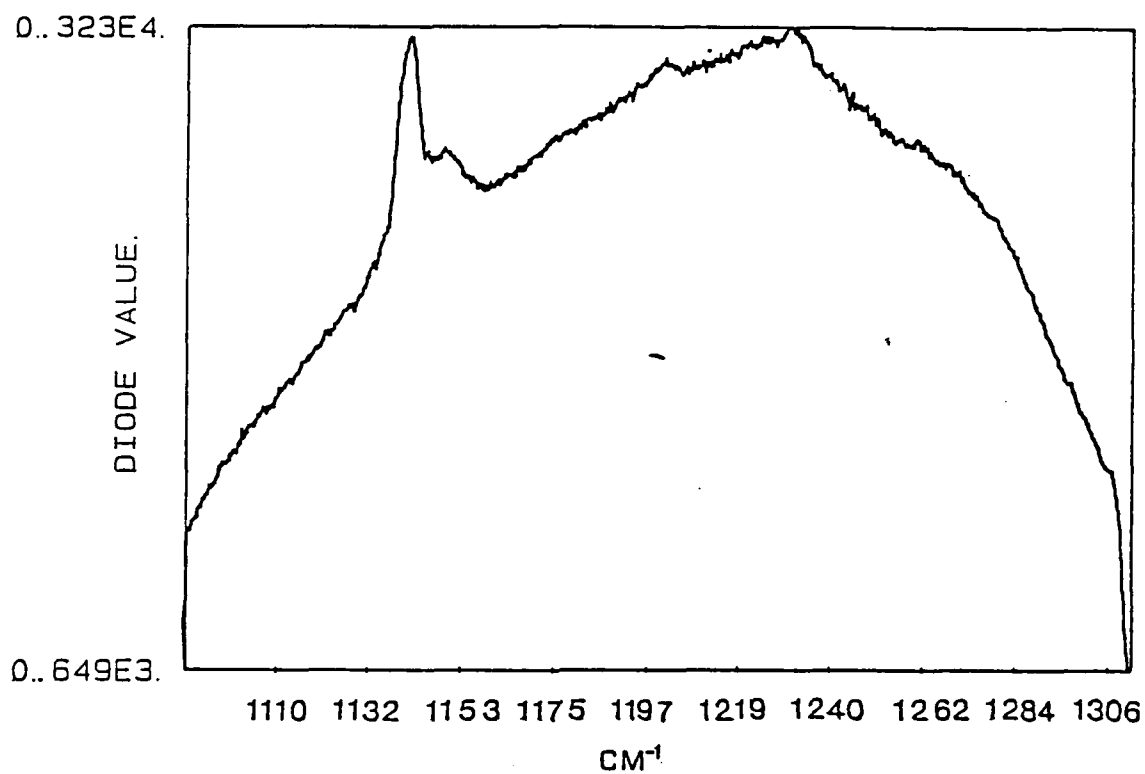


Fig. 9. Raman spectrum of 1M $\text{Ca}(\text{AlCl}_4)_2$ -TC+30% (v/v) SO_2 at room temperature.

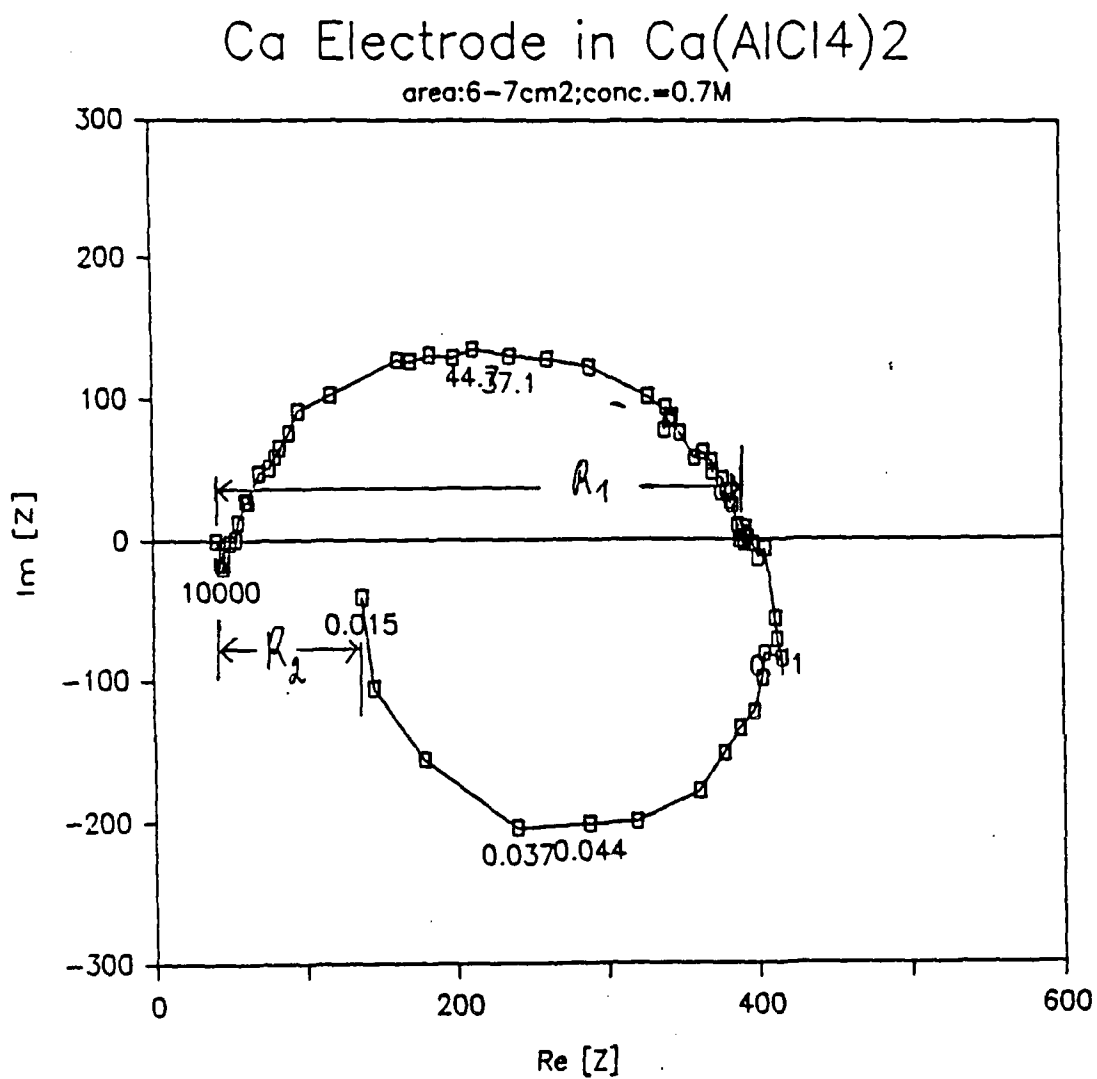


Fig. 10. An AC spectrum for Ca electrode in 0.75M $\text{Ca}(\text{AlCl}_4)_2$ - SOCl_2 solution after four days of storage at room temperature.

To date no funds have been received from U.S. Army on this contract.

During this period we have already incurred expenses as per budget of this contract.

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